

# The role of screening in the density functional applied on transition metal defects in semiconductors

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We study selected transition metal related point defects in silicon and silicon carbide semiconductors by a range separated hybrid density functional (HSE06). We find that HSE06 does not fulfill the generalized Koopmans' Theorem for every defect which is due to the self-interaction error in the functional in such cases. Restoring the so-called generalized Koopmans' Condition with a simple correction in the functional can eliminate this error, and brings the calculated charge transition levels remarkably close to the experimental data as well as to the calculated quasi-particle levels from many-body perturbation theory.

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Tractable solutions for the problem of many-electron systems are highly needed in materials science and under intense research. One key example of such problems is the treatment of small imperfections in single crystals, i.e. point defects in semiconductors. Point defects can completely change *locally* the chemical bonds of the host crystal, thus *ab initio* methods are needed in order to determine their geometry, electronic structure, ionization energies or optical excitations. The most challenging type of point defects is the transition metal (TM) related defects in traditional semiconductors where *d*-orbitals tightly localized on the TM atoms and *sp*<sup>3</sup> hybrid orbitals are both present in the system. It is known from , e.g. studies of Mott-insulators that *d*-electron systems may be highly correlated whereas the electronic structure of traditional semiconductors can phenomenologically be well-described by independent particle theories. Simulations of TM defects in semiconductors are therefore a complex problem, thus it is an obvious system to investigate the predictive power of the *ab initio* methods.

Density functional theory (DFT) is the most widespread technique for first principles calculation in condensed matter physics. Particularly, DFT has been proven to be extremely powerful tool to study defects in semiconductors [1]. The success of the DFT calculations is based on well-developed approximate (semi)local functionals [2–5] that made it possible to study relatively large systems at moderate computational cost with a surprisingly good accuracy [1]. The success of the commonly used (semi)local functionals might be unexpected as they suffer from the self-interaction error [3] which results in the underestimation of the band gap of semiconductors. The predictive power of (semi)local functionals is thus restricted for ionization energies of defects in semiconductors, and can even fail to describe the nature of the host semiconductor, or the defect state in the semiconductor correctly in pathological cases [6–8]. By mixing a non-local Fock exchange into the density functional, i.e., by using hybrid density functionals, one can restore the band gap of host semiconductors via tuning the mixing parameter [9–13]. Alternatively, by introducing a range separated hybrid density functional (HSE06) it is found that with a fixed mixing parameter and the range of separation, the band gap of many

semiconductors with *sp*<sup>3</sup> hybrid orbitals can be well reproduced [14], and in addition, the structural parameters, redox reaction energies, and formation energies of transition metal compounds can also be well accounted by HSE06 [15]. This brings a hope that HSE06 is able to predict the ground state [16] and ionization energies for TM related defects in semiconductors which contain both *d* and *sp*<sup>3</sup> orbitals. However, a consistency of the approach requires the use of the same mixing and range separation parameters for the host and impurity states. It has been observed that this requirement makes it difficult to describe band structure and defect states simultaneously [17, 18].

In this *Letter* we study TM defects in silicon (Si) and 4H silicon carbide (SiC) semiconductors by HSE06 functional using plane wave large-supercell calculations, for those experimental data about their structure and ionization energies are available. We show that HSE06 can qualitatively fail in such complex systems due to insufficient screening of the Coulomb interaction between localized *d*-electrons, leading to incomplete cancelation of the self-interaction error which manifests as disobeying the generalized Koopmans' Theorem (gKT) [7, 17, 19, 20]. We suggest a correction scheme for the hybrid functional which fulfills the conditions of gKT. The corrected functional allows for a simultaneous description of localized and extended states, is first-principles in nature, and brings our theoretical results remarkably close to the experimental data as well as to the results obtained by means of many-body perturbation theory. Our work underlines the importance of testing a fulfillment of gKT for the applied functionals on a given many-electron system.

We selected interstitial Fe in Si (Fe<sub>i</sub>), and titanium (Ti<sub>Si</sub>), vanadium (V<sub>Si</sub>) and chromium (Cr<sub>Si</sub>) substituting Si-site in 4H SiC. For all of these defects, the structure and the corresponding ionization energies are well established from experiments [21–23, 25]. In addition, we investigate tungsten (W) in 4H SiC because W-related ionization energies have been detected recently [24]. In this case, the origin of the W-related centers are not ambiguously identified. According to our previous study [26], both Si-substitution site (W<sub>Si</sub>) and asymmetric split vacancy configuration (W<sub>ASV</sub>) may be stable, thus both defects are considered. For the electronic structure

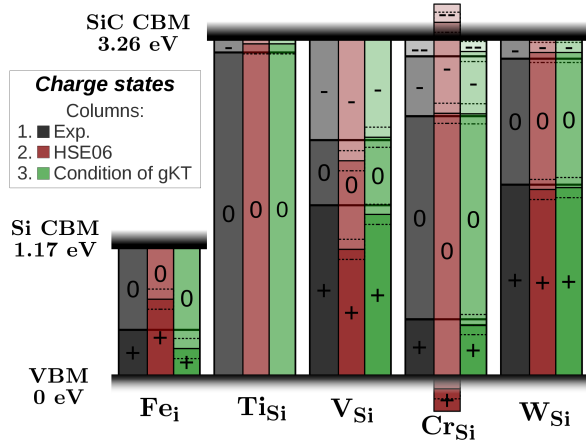


FIG. 1. (Color online) Measured and theoretically predicted charge transition levels of transition metal impurities in 4H SiC and Si hosts. In all cases the experimental results [21–24] are represented with dark gray (first) columns where the thick horizontal line represents the charge transition levels. The result of HSE06 calculations and our correction method with satisfying gKT are represented with red (second) columns and light green (third) columns, respectively, where thin horizontal lines provide the calculated charge transition levels. The bars indicated by dashed lines around the calculated charge transition levels show the inherent uncertainty of the calculation. Chromium needs special consideration regarding the (0|-) transition level, see text.

calculations we use VASP package [27] with plane wave basis (cut-off: 420 eV) and projector augmented-wave (PAW) [28] method for the ion-cores. In the case of metal atoms we utilize small core PAW projectors. In order to model 4H SiC and Si host we use a 576-atom and 512-atom supercells, respectively. In the large supercells the Brillouin zone is sampled at  $\Gamma$ -point. In the case of charged defects the size dependence of total energies is eliminated by charge correction [29] with the order of magnitude 0.1 eV in our supercells. The geometry of the defects is optimized unless the forces acting on the atoms are less than 0.01 eV/Å.

In order to examine the performance of the HSE06 screened non-local hybrid density functional on the selected transition metal defects in semiconductors we calculate the adiabatic ionization energies or charge transition levels of these defects,

$$\varepsilon(q|q') = (E_{q'} + E^{\text{corr}}(q')) - (E_q + E^{\text{corr}}(q)) - \varepsilon_{\text{CBM}} \quad (1)$$

where  $E_q$  is the total energy and  $E^{\text{corr}}(q)$  is the charge correction of charge state  $q$  and  $\varepsilon_{\text{CBM}}$  is the conduction band minimum (see Ref. 1 for more details). The HSE06 functional gives the proper description of the band structure of the semiconductor host. The band gap error is within 0.1 eV for the pristine 4H SiC and Si host which causes uncertainty in the calculated  $\varepsilon(q|q')$  of about 0.1 eV. By comparing the experimental data with the results of HSE06 calculations it is apparent from Fig. 1 and Table I that HSE06 cannot predict the correct charge transition levels for all the defects. The magnitude of the discrepancies depend on the TM as well as the charge

TABLE I. (Color online) Experimental values of charge transition levels ( $\varepsilon_{\text{exp}}$ ), deviations of the theoretically predicted values from the experiment for transitional metal related point defects,  $\text{Ti}_{\text{Si}}$ ,  $\text{V}_{\text{Si}}$ ,  $\text{Cr}_{\text{Si}}$  and  $\text{W}_{\text{Si}}$  in 4H SiC and  $\text{Fe}_{\text{i}}$  in Si. In the calculations HSE06 functional and a corrected HSE06 functional (see text) are used. The finite values of  $E_{\text{NK}}$  clearly indicates the presence of self-interaction error in the HSE06 functional ( $\Delta\varepsilon_{\text{HSE06}}$ ). When small value of  $E_{\text{NK}}$  is obtained ( $E'_{\text{NK}}$ ) with the help of additional correction functional ( $V_w$ ) with a strength parameter  $w$ , the discrepancy ( $\Delta\varepsilon_{\text{HSE06}+V_w}$ ) goes below 0.1 eV which is the uncertainty in our calculation. Light red (dark green) numbers represent the case when the calculated charge transition level is out of (within) the error bar. The unit of the data is eV in all columns.

Transition	$\varepsilon_{\text{exp}}$	$E_{\text{NK}}$	$\Delta\varepsilon_{\text{HSE06}}$	$w$	$E'_{\text{NK}}$	$\Delta\varepsilon_{\text{HSE06}+V_w}$
$\text{Ti}_{\text{Si}} : (0 -)$	-0.12 <sup>a</sup>	-0.02	+0.01	0.0	-0.02	+0.10
$\text{V}_{\text{Si}} : (+ 0)$	-1.60 <sup>a</sup>	-0.91	-0.43	-2.7	+0.02	-0.09
$\text{V}_{\text{Si}} : (0 -)$	-0.97 <sup>a</sup>	-0.81	-0.20	-2.2	+0.02	+0.03
$\text{Cr}_{\text{Si}} : (+ 0)$	-2.70 <sup>a</sup>	—	VB	-3.0	-0.00	-0.05
$\text{Cr}_{\text{Si}} : (0 -)$	-0.74 <sup>a</sup>	-0.21	+0.02	—	—	+0.01
$\text{Cr}_{\text{Si}} : (- 2-)$	-0.18 <sup>a</sup>	-1.88	+1.85	-6.0	+0.01	+0.05
$\text{W}_{\text{Si}} : (+ 0)$	-1.40 <sup>b</sup>	-0.13	-0.05	-1.2	+0.01	-0.03
$\text{W}_{\text{Si}} : (0 -)$	-0.18 <sup>b</sup>	-0.03	+0.06	0.0	-0.03	+0.06
$\text{Fe}_{\text{i}} : (+ 0)$	-0.79 <sup>c</sup>	-0.68	+0.32	-3.8	-0.09	-0.15

<sup>a</sup> Ref. [22], <sup>b</sup> Ref. [24], <sup>c</sup> Ref. [21]

transition level (Table I). Particularly, the calculated ionization energies of Cr strikingly differs from the experimental values, and are *qualitatively* wrong.

Let us demonstrate that the failure of HSE06 for some defects originates from the incorrect treatment of atomic-like  $d$ -orbitals of TM atoms. It is well-known that self-Hartree and the exchange potentials do not cancel each in (semi)local DFT functionals. In (semi)local functionals the resultant self-repulsive potential lower the localization degree of the states and cause the spurious occupation dependence of the Kohn-Sham energies as well as the spurious, generally convex, curvature of the total energy with respect to fractional occupations [7, 19, 20]. The opposite behavior is characteristic for Hartree-Fock (HF) method. By mixing HF and semi-local exchange, the self interaction error is reduced in hybrid functionals. Unfortunately, it is not eliminated completely.

Previous studies show [7, 17, 19, 20] that one of the quantitative manifestation of the self-interaction error in DFT functionals is the discrepancy between the Kohn-Sham eigenvalue of the highest occupied state and the corresponding ionization energy. This energy difference is usually called as Non-Koopmans' energy,

$$E_{\text{NK}} = \varepsilon_N - E_I = \varepsilon_N - (E_N - E_{N-1}) \quad (2)$$

where  $\varepsilon_N$  is the Kohn-Sham energy of a localized state in  $N$  electrons system,  $E_I$  is the ionization energy of the system which equal to the difference of the total energies of the  $N$  electron,  $E_N$ , and  $N - 1$  electron system,  $E_{N-1}$ . In HF theory the Koopmans' Theorem states that the single particle energies equal to the ionization energy in case of every oc-

cupied states, while in DFT this statement is only valid for the highest occupied state with an exact exchange-correlation functional. In the case of exact functional  $E_{\text{NK}} = 0$  condition should be fulfilled, the so-called generalized Koopmans' Condition (gKC). Due to the Janak's and Slater's theorems, other important features of the exact functional is simultaneously remedied: linear behavior of the total energy and constant behavior of (highest occupied) single particle level with respect to fractional occupation are also fulfilled. The last condition explicitly shows that the single particle state does not suffer from any occupational dependent potential, thus represents a self-interaction free functional.

In Table I one can see the difference in the calculated HSE06 results and experimental data as well as the calculated Non-Koopmans' energy for the defect state that gets occupied through the charge transition. In the calculation of  $E_{\text{NK}}$  we considered the two charge states of the defect with fixing the geometry as found in the first charge state. The results clearly show that this quantity correlates with the discrepancy between HSE06 results and experimental data for the charge transition levels. The obvious conclusion of this finding is that the errors are originated from the spurious self-interaction which still remains in the HSE06 functional.

In HSE06 functional, the mixing parameter and the range of separation play the role of effective screening of Coulomb interaction [30–32], and their variation in practice interpolates between the substantial underestimation of the localization effects in (semi)local functionals and their overestimation in Hartree-Fock theory. But the strength of the screening should itself depend on the localization degree of the states. In the case of TM impurities the strong repulsive interaction between the electrons stems the extension of the atomic-like electron states. In such a strongly correlated system, the localized states are more favorable than the extended one. Due to the large localization degree of the  $d$ -states with respect to that of host  $sp^3$  hybrid orbitals, in general it should not be possible to describe both subsystems with the same values of parameters in a hybrid functional. Lany and Zunger [17] demonstrated that one should not expect that adjusting parameters of hybrid functionals would automatically give accurate results for both, host band gaps and defect levels, and pointed out homogeneous screening of the Fock exchange in hybrid functionals as serious simplification. Still, it is desirable to have an option to describe the orbitals with different degrees of localization in calculations.

At this stage, it is important to mention that, a systematic study of the role of nonlocal exchange in the electronic structure of correlated oxides by F. Iori *et al.* [32] demonstrates that the default values of parameters of HSE06 functional systematically *overestimate* band gaps in these materials, indicating insufficient screening of Coulomb interaction. Negative values of  $E_{\text{NK}}$  in Table I also indicate that the screening of Coulomb interaction is insufficient [17].

In order to prove the self-interaction error of HSE06 functional, we carry out sophisticated parameter free  $\text{GW}_0$  calculations [33] on defective supercells with 128 atoms and

TABLE II. The position of the highest occupied single particle levels of transitional metal defects in the gap with respect to the conduction band edge (CBM) in eV unit. The table shows the results of calculations with  $\text{GW}_0$  method, HSE06 functional and corrected HSE06 functional (HSE06+ $V_w$ ). In the case of  $\text{Cr}_{\text{Si}}(0)$  the corresponding single particle state falls in the valence band shown as “VB”, thus  $\text{GW}_0$  started far from the true ground state of the system. When Non-Koopmans' energy ( $E_{\text{NK}}$ ) is not negligible the correction method as well as the  $\text{GW}_0$  method shift the levels up with approximately the same value. This result confirms the presence of self-interaction error in the HSE06 functional and validate our corrected functional.

Defect	$\text{GW}_0$	HSE06	HSE06+ $V_w$
$\text{V}_{\text{Si}}(0)$	-1.86	-2.79	-1.94
$\text{V}_{\text{Si}}(-)$	-1.21	-2.19	-1.50
$\text{W}_{\text{Si}}(0)$	-1.66	-1.85	-1.68
$\text{W}_{\text{Si}}(-)$	-0.94	-0.83	-0.83
$\text{Cr}_{\text{Si}}(0)$	-3.22	VB	-2.83
$\text{Cr}_{\text{Si}}(-)$	-0.74	-1.00	–
$\text{Cr}_{\text{Si}}(2-)$	+0.07	-0.49	-0.17

HSE06 relaxed geometry. We apply 1344 bands in the calculation of the response function, and the Brillouin zone is sampled with  $2 \times 2 \times 2$  Monkhorst-Pack  $k$ -point set [34]. The starting wave functions are obtained from HSE06 calculation, then the Green-function  $G$  and the wave functions are self-consistently updated while keeping the screened Coulomb-interaction  $W$  fixed. We find that four iterations are sufficient to reach the self-consistent quasi-particle levels within 0.05 eV. The observed quasiparticle correction (see Table II) confirmed the over-localization error of the HSE06.

Considering  $E_{\text{NK}}$  is an appropriate measure to construct a self-consistent correction method to eliminate the self-interaction error in the functional [7, 19], we propose a scheme that does not use any empirical parameters to counteract the error due to insufficient screening of the Coulomb interaction between  $d$ -electrons localized at TM related defects, which is apparently present in HSE06 functional.

In our correction technique the occupation dependent potential

$$V_w^{Im} = \frac{w}{2} (1 - 2n_m^I) \quad (3)$$

is applied on the  $d$ -orbitals together with the screened non-local HSE06 functional. In Eq. (3)  $w$  is a parameter for the strength of the potential, which physical meaning will become clear below, and which is determined self-consistently by satisfying gKC. We emphasize that the resultant functional is *ab initio* in the sense that it is not fit to any empirical parameter. We note that the form of Eq. (3) is equivalent to Dudarev's implementation of LDA+U method [35], and therefore it is straight-forward to use the suggested scheme with existing first-principles package like VASP. The occupation number  $n_m^I$  in VASP implementation is determined as projection of the wave function of the system on the spherical harmonics  $lm$  on site of atom  $I$ , where  $l = 2$  in our case.

The results are summarized in Table I. One sees that gKC could be fulfilled with great accuracy ( $E'_{\text{NK}}$ ) in all cases except for  $\text{Fe}_i$  in Si and  $\text{Cr}_{\text{Si}} : (0|-)$  in SiC. In case of iron  $E_{\text{NK}}$  has an extrema and does not reach zero. We observed that the particular defect state is not so well localized on the Fe  $d$ -orbital in  $\text{Fe}_i$  defect, thus our correction scheme is not sufficiently effective. Similar effect can be found in case of negatively charged  $\text{Cr}_{\text{Si}}$  where in the ground state three electron occupy the  $e$  and  $a_1$  levels with parallel spins. The highest occupied  $a_1$  level is also less atomic-like compared to the  $e$  level. In Table I the  $\text{Cr}_{\text{Si}} : (0|-)$  charge transition level is calculated as  $\varepsilon_{\text{GW}} + E^{\text{relax}} + E^{\text{corr}}$ , where  $\varepsilon_{\text{GW}}$  is the highest occupied quasi-particle level in the negative charge state, and  $E^{\text{relax}}$  is the relaxation energy of the defect due to ionization [36]. Note that achieving gKC with a certain accuracy brings the corrected single particle level to be independent from the occupation number with the same accuracy indicating the self interaction free description of the defect state. The charge transition level was obtained after the geometry relaxation of system with the use of the corrected HSE06+ $V_w$  functional shown in the last column of Table I. Apparently, this correction method can bring the theoretical values closer to the experimental values in every case. When gKC is accurately satisfied the calculated levels approach the experimental levels within 0.1 eV which is the expected uncertainty in our calculation. It also can be seen that when gKC is fulfilled the position of the defect state in the gap is close to the corresponding quasi-particle level calculated by the  $\text{GW}_0$  approximation of the many-body perturbation theory. We note here that the formation energies of the defects are also affected by our correction scheme which is discussed in the Supplemental Material [36].

Considering the strength of the required correction potentials an important remark can be made. In all the cases when the correction is needed, the parameter  $w$  is negative representing a repulsive potential for occupied states. This observation confirms that HSE06 functional over-localizes the defect state of the TM impurities, while this spurious effect is eliminated with our technique. In more details this is illustrated in Fig. 2(b) where the difference of the spin density of HSE06 and HSE06+ $V_w$  calculation is shown. In the case of TM impurities, the HSE06 functional clearly represents an over-correction with respect to standard (semi)local DFT functionals.

In order to understand the physical meaning of parameter  $w$  in Eq. (3), we will make use of the similarity between the way how hybrid functionals and LDA+U approach [35, 37, 38] correct the self-interaction error, pointed out by several groups [32]. For the case of correlated electrons it becomes particularly apparent within the so-called exact exchange for correlated electrons method by Novak and co-workers [39]. LDA+U functional was introduced in order to take into account the effects of the strong correlation which is usually not properly described by (semi)local functionals [35, 37, 38].

The positive value of the Hubbard parameter  $U$  representing the strength of the *screened* Coulomb potential makes the

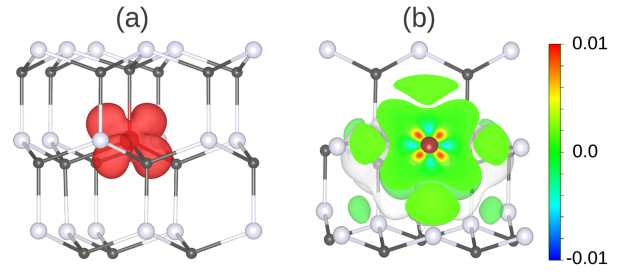


FIG. 2. (Color online) (a) The calculated electron density (with an isosurface value of 0.05) of the unpaired  $d$ -orbital of the neutral vanadium substitutional defect in  $4H$  SiC. (b) 2D plot of the differences between two calculated charge densities using HSE06 functional and the corrected HSE06 functional around the vanadium atom. The positive finite density clearly represents the overlocalization error of the HSE06 functional.

atomic like states more favorable and increase the localization of the states on atomic orbitals. In practice the screening of  $U$  is achieved by a reduction of the large bare Coulomb value, and the actual strength of the on-site electron repulsion can be either determined empirically [40, 41], or evaluated *ab initio* [42, 43]. As a matter of fact, in our case of the TM defects the Coulomb interaction between localized electrons (Fig. 2) appears to be insufficiently screened in HSE06 functional due to its homogeneous nature and parameters adjusted to describe more extended states. In LDA+U formalism this error could be corrected by a reduction of  $U$  parameter. Employing the above mentioned similarity between the hybrid functionals and LDA+U method, we see that the action of occupation dependent potential in Eq. (3) on localized orbitals at impurity sites effectively increases the screening of Coulomb interaction between electrons occupying these orbitals.

Finally, we show the predictive power of our methodology demonstrated on W-related defects in  $4H$  SiC. We find that  $\text{W}_{\text{Si}}$  defect has two charge transition levels and these are very close to the experimental values. In the case of  $\text{W}_{\text{ASV}}$  defect HSE06 again suffers from the self-interaction error,  $E_{\text{NK}} = -0.18$  eV, and correction is needed in the functional with  $w = -2.4$  eV. It is worthy to notice that this value differs from the value needed for  $\text{W}_{\text{Si}}$  defect which shows that the self-interaction error for TM defects may be different in various defect configurations. With our correction method the  $(0|-)$  charge transition level of  $\text{W}_{\text{ASV}}$  defect is at  $\varepsilon_{\text{CBM}} - 0.64$  eV where no W-related charge transition level was found in the experiments (see Table I). This indicates that  $\text{W}_{\text{Si}}$  is associated with the measured W-related center [24], thus we show the calculated ionization energies of  $\text{W}_{\text{Si}}$  in Table I.

In summary, our theoretical investigation revealed that the HSE06 hybrid functional may overlocalize the defect states arisen from transition metal defects. The reason of this error is the self-interaction that is increased due to the insufficient screening of Coulomb interaction between electrons localized at the transitional metal defects. By invoking the generalized Koopmans' Condition we were able to indicate the

presence of self-interaction error in the calculation. Furthermore, we suggest a correction method which can eliminate the self-interaction error of hybrid functionals in the case of atomic-like defect states. With this technique all the calculated charge transition levels become accurate within 0.1 eV. In addition, the corrected Kohn-Sham levels are close to those obtained by the sophisticated but computationally demanding GW<sub>0</sub>-method.

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# Supplemental Material

for the paper entitled

The role of screening in the density functional applied on transition metal defects in semiconductors

by

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## 1. Calculation methods

For the electronic structure calculations we use VASP package [R1] with plane wave basis (cut-off: 420eV) and projector augmented-wave (PAW) [R2] method for the ion-cores. In the case of metal atoms we utilize small core PAW projectors. In order to model 4H SiC and Si host we use a 576-atom and 512-atom supercells, respectively. In the large supercells the Brillouin zone is sampled at  $\Gamma$ -point. In the case of charged defects the size dependence of total energies is eliminated by charge correction [R3] with the order of magnitude 0.1~eV in our supercells. The geometry of the defects is optimized unless the forces acting on the atoms are less than 0.01eV/Å.

GW calculations are carried out in 128-atom supercell where HSE06 relaxed geometry is applied in defective supercells. We apply 1344 bands in the calculation of the response function, and the Brillouin zone is sampled with 2×2×2 Monkhorst-Pack  $k$ -point set [R4]. The starting wave functions are obtained from HSE06 calculation, then the Green-function  $G$  and the wave functions are self-consistently updated while keeping the screened Coulomb-interaction  $W$  fixed. We find that four iterations are sufficient to reach the self-consistent quasi-particle levels within 0.05 eV.

## 2. Relative stability and charge transition level diagram

Our method is designed to correct a localized atomic like single particle orbital by recovering its real charge density. Accurate charge transition levels can be obtained from the sum of the vertical ionization energy obtained from the generalized Kohn-Sham level and the geometry relaxation energy due to ionization (See Fig. S1 and Table SI in paper). The necessary correction on the Kohn-Sham level depends on the given transitional metal (TM) as well as on the total occupation number of the  $d$ -like

states of this TM-atom, or in other words, on the charge state of the defect. Due to the varying additional screening functional the total energy will be not “unique”. The main difficulty may arise from this method when the total energies of different configurations of the given TM impurity are compared in order to determine their relative stability.

To overcome this difficulty, it is possible to choose a common screening parameter  $w_c$  for two or more neutrally charged defects. A rational choice is the average of the parameters  $w$  obtained for different configurations of the given TM impurity, however it is unknown how sensitive is the relative stability to the choice of the common parameter  $w_c$ .

We studied the formation energies of the experimentally most relevant TM defects in 4H-SiC. We considered the substitutional defect ( $\text{TM}_{\text{Si}}$ ) at  $h$  site and the asymmetric split vacancy defect (ASV), consisting of  $\text{TM}_{\text{Si}}$  and a carbon vacancy ( $\text{TM}_{\text{Si}}\text{-V}_\text{C}$ ) at  $hh$  site when TM is V or W.

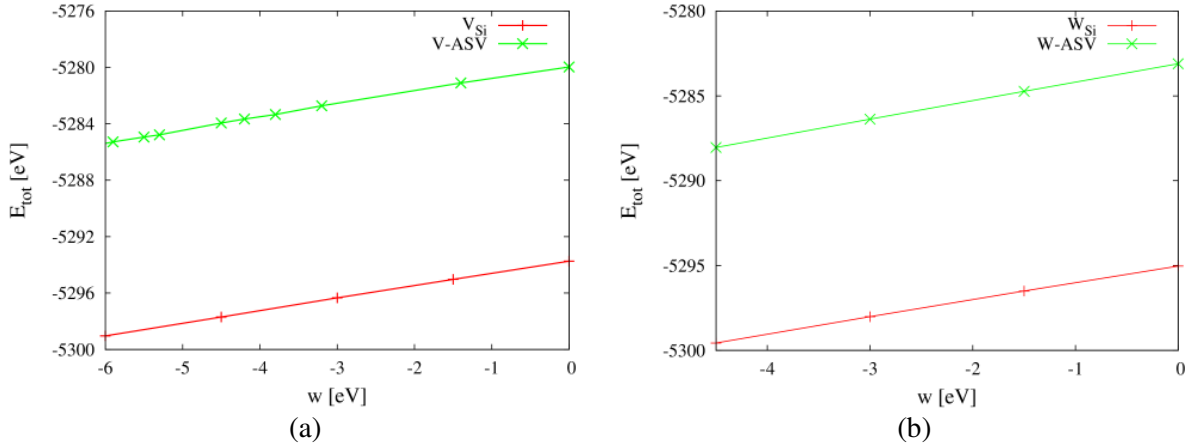


FIG. S1. (Color online) The total energy ( $E_{\text{tot}}$ ) of substitutional and ASV defects of neutral (a) vanadium (V) and (b) tungsten (W) is plotted as a function of the applied screening potential ( $w$ ).

The total energies of the two types of TM-defect with respect to screening parameter  $w$  can be seen in Figs. S1(a) and (b). Total energies depend linearly on the parameter  $w$  and, in addition, the slope of the curves is close to each other, for example 0.912 for V-ASV and 0.885 for  $V_{\text{Si}}$ . Due to this behavior the relative stability is approximately (within  $\sim 0.1$  eV) independent on the choice of the common screening parameter  $w_c$  and is close to results of HSE06 calculation. In critical cases (e.g. when the difference in total energies is close to 0.1 eV), the hierarchy may change as a function of  $w$  parameter. W impurity is such an example in 4H SiC.

The obtained screening parameter and the corrected charge transition levels for the considered defects are summarized in Table S1.

TABLE SI. The optimized screening parameter  $w$  that fulfill the gKC and the corresponding corrected charge transition levels with respect to the conduction band edge ( $\Delta E_{\text{HSE06}+V_w}$ ) of substitutional and ASV defects of V and W.

defect	$w$ [eV]	$\Delta E_{\text{HSE06}+V_w}$ [eV]
$V_{\text{Si}} : (+ 0)$	− 2.7	− 1.69
$V_{\text{Si}} : (0 -)$	− 2.2	− 0.94
$V\text{-ASV} : (+ 0)$	− 4.6	− 1.47
$V\text{-ASV} : (0 -)$	− 4.2	− 1.29
$W_{\text{Si}} : (+ 0)$	− 1.2	− 1.43
$W_{\text{Si}} : (0 -)$	0.0	− 0.12
$W\text{-ASV} : (+ 0)$	− 2.6	− 2.44
$W\text{-ASV} : (0 -)$	− 2.4	− 0.64

The chosen common parameters and the corresponding relative stability at Si-rich condition can be found in Table SII. With this data it is possible to draw the transitional level diagram which shows the relative stability with respect to the Fermi-level (Figure S2). We note that the HSE06+ $V_w$  functional with the use of common  $w_c$  parameter produces superior results in comparison to conventional calculations using HSE06 functional.

TABLE SII. The chosen common screening parameters  $w_c$  for the pair of substitutional and ASV defects of V and W. The relative stability ( $E_{\text{rel}}$ ) of neutral defects is shown as obtained by HSE06 and HSE06+ $V_w$  functionals.

defect pairs	$w_c$ [eV]	$E_{\text{rel,HSE06}}$ [eV]	$E_{\text{rel,HSE06}+V_w}$ [eV]
$V_{\text{Si}} - V\text{-ASV}$	− 3.65	1.82	1.87
$W_{\text{Si}} - W\text{-ASV}$	− 1.9	0.03	− 0.15



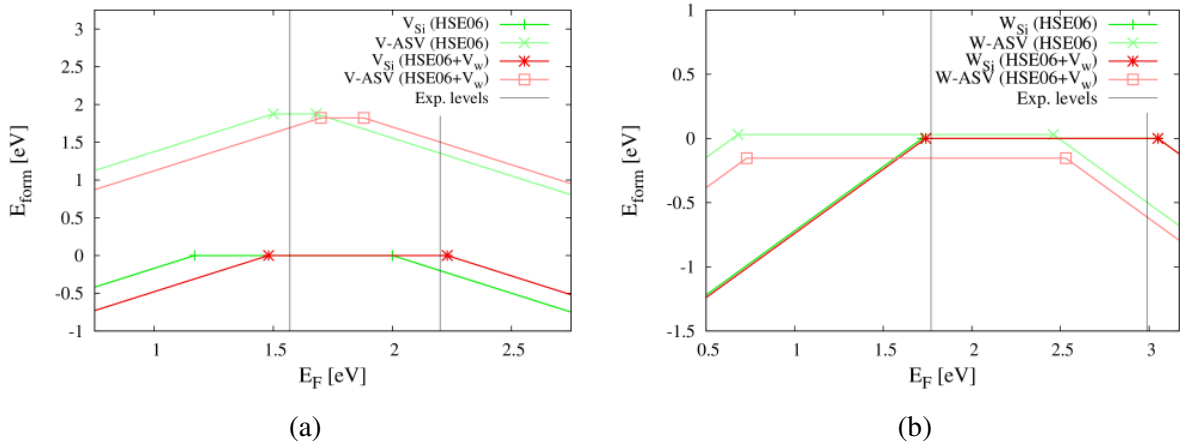


FIG. S2. (Color online) Charge transition level diagram of two different types of defect of vanadium (V) (a) and tungsten (W) at Si-rich condition as obtained by HSE06 and HSE06+ $V_w$  functionals (see text). Black vertical lines represent the position of the experimental charge transition levels. The formation energy of the substitutional defect was set to zero as a reference energy in both cases.

### 3. Partial density of states

Partial density of states of neutrally charged substitutional vanadium in 4H-SiC is plotted in Fig. S3. Calculations are carried out using both HSE06 and HSE06+ $V_w$  functionals. In the case of vanadium ( $V^{4+}$ ) there is only one electron to occupy the lowest double degenerate  $d$ -like state ( $e$ ) that splits into two non-degenerate levels in  $C_{1h}$  symmetry. The major spin channel is chosen to be the spin-up channel. In the major spin channel both states appear in the gap, the lowest is occupied and the other one is unoccupied as the Fermi-level is at 0.37 eV and 1.27 eV in HSE06 and HSE06+ $V_w$  calculations, respectively. The states are slightly hybridized with the  $s$  and  $p$  orbitals of the host semiconductor. The other  $d$ -states, however, are so strongly hybridized with the  $s$  and  $p$  orbitals that they lose their atomic character. This is particularly apparent for the occupied states below the Fermi-level [see Fig. S3(c)] while empty resonant  $d$ -states may occur in the conduction band. The effect of the correction potential on those states is almost negligible but very strong on the states occurring in the band gap.

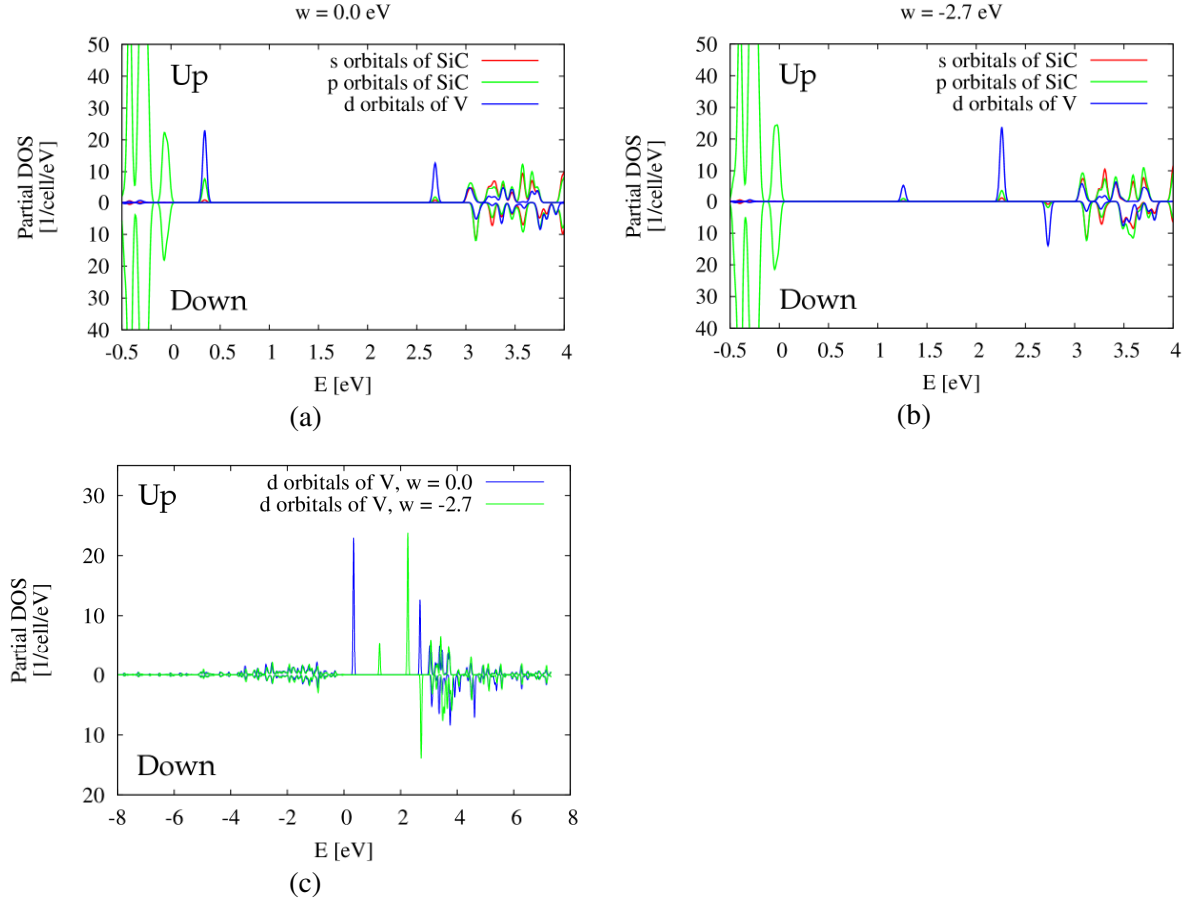


FIG. S3. Partial density of states substitutional vanadium in 4H-SiC calculated by (a) HSE06 functional and (b) and HSE06+ $V_w$  functional close to the Fermi-level; (c) by HSE06 and HSE06+ $V_w$  functional in wide energy range. The energy of the valence band edge was chosen to zero as reference. Up(down) labels the spin-up(down) channel. The spin-up channel is the majority spin channel. The calculated Fermi-level is at 0.37 eV and 1.27 eV in HSE06 and HSE06+ $V_w$  calculations, respectively.

#### 4. Calculation of the electronic structure of chromium

We mention here that chromium (Cr) defect needs special consideration in determining  $w$ . In the ground state of the negatively charged  $\text{Cr}_{\text{Si}}$  defect a double degenerate  $e$  level and an  $a_1$  level appear in the gap, originated from the split  $d$ -orbitals of Cr in the crystal field of 4H-SiC with  $C_{3v}$  symmetry. In the neutral charge state two electrons occupy the  $e$  state while the  $a_1$  state is empty, forming  $S = 1$  spin state. Due to the strong correlation of the  $d$ -orbitals  $S = 3/2$  state is formed in the negatively charged state where three electrons occupy the  $e$  and  $a_1$  levels with parallel spins. In the negatively charged state, our correction method acts on the highest occupied  $a_1$  level which is less atomic like compared to the  $e$  level. Our correction method makes the atomic-like defect states more or less favorable therefore

changes the charge density in a way that changes the character of the  $a_1$  level. In Table I of the main text the  $\text{Cr}_{\text{Si}}:(0|-)$  charge transition level is calculated as  $\epsilon_{\text{GW}} + E^{\text{relax}} + E^{\text{corr}}$ , where  $\epsilon_{\text{GW}}$  is the highest occupied quasi-particle level in the negative charge state, and  $E^{\text{relax}}$  is the relaxation energy of the defect due to ionization. In the case of the  $\text{Cr}_{\text{Si}}:(-|2-)$  transition, the  $a_1$  level becomes empty and the  $e$  level gets fully occupied by ionizing from  $(-)$  to  $(2-)$  states. Here, we set  $S = 1/2$  instead of the energetically favorable  $S = 3/2$ , for the initial negative charge state in order to be able to study of the effect of the occupation of  $e$  level and to correct its level *via* satisfying gKC with our correction functional.

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SiC CBM  
3.26 eV

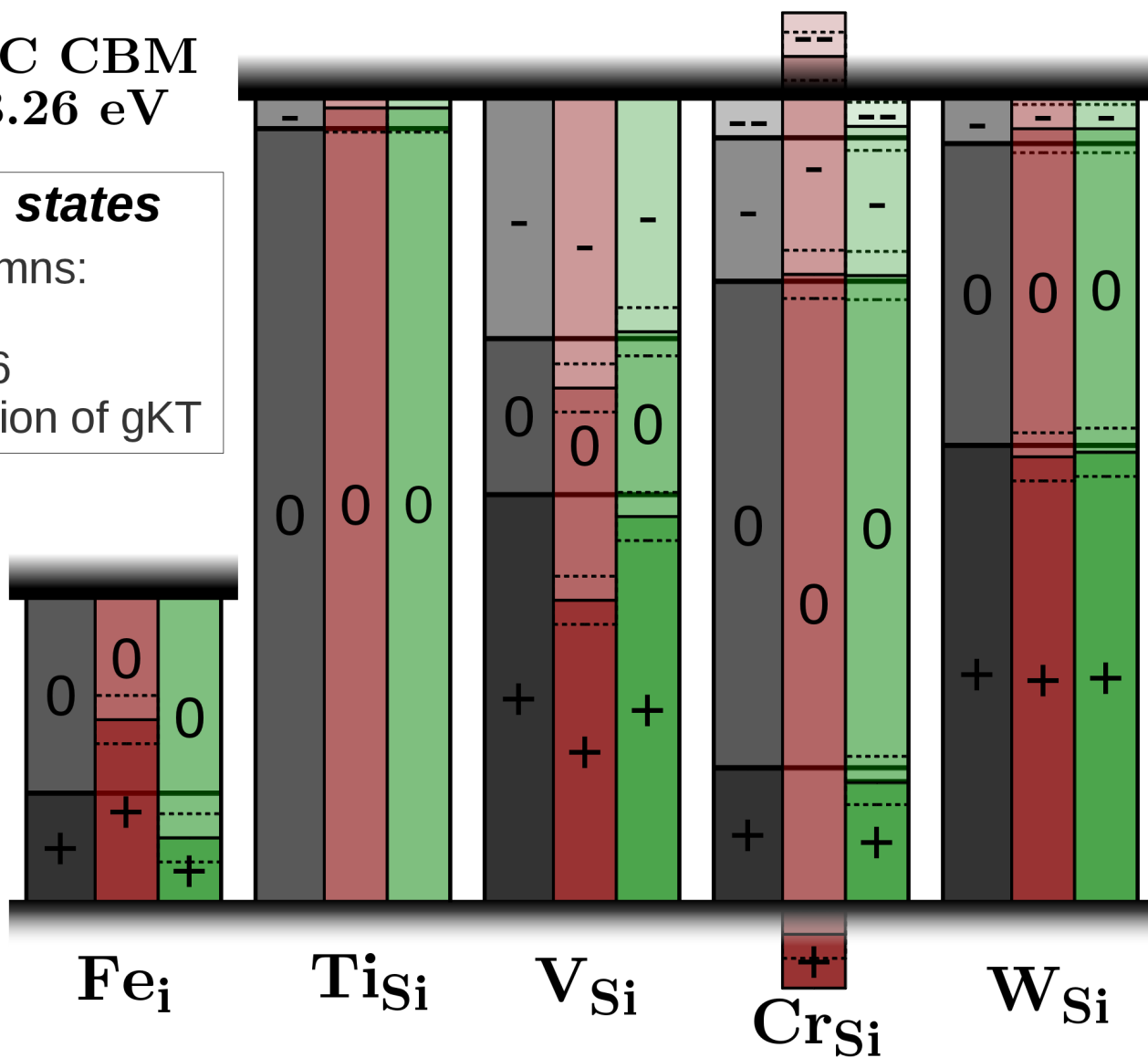
### Charge states

Columns:

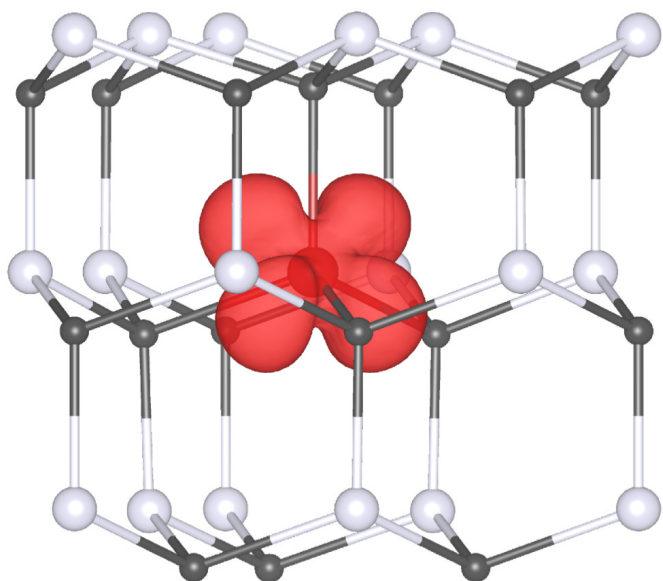
1. ■ Exp.
2. ■ HSE06
3. ■ Condition of gKT

Si CBM  
1.17 eV

VBM  
0 eV



(a)



(b)

